

COMPARISON OF METHODS FOR DETERMINING ASPHALTENES IN
COAL-DERIVED LIQUID FUELS

H. Schultz and M. J. Mima

DEPARTMENT OF ENERGY
PITTSBURGH ENERGY RESEARCH CENTER
4800 Forbes Avenue
Pittsburgh, Pennsylvania 15213

There is at present no standard method for the determination of asphaltenes in the products of coal conversion, nor is there any known relationship between the values for asphaltene concentration produced by the various analytical methods currently in use. Lacking a standard method of analysis, are comparisons of the coal conversion products of the various processes possible? The research described in this paper attempts to answer this question at least in part.

Five different solvent separation methods which are currently in use for determining asphaltenes in coal-derived liquids have been studied in the analytical chemistry laboratory of the Pittsburgh Energy Research Center of the U. S. Department of Energy. The material chosen for the tests was a liquid product which was produced from the Center's 0.5 ton-per-day hydrodesulfurization plant. The material was produced using a fixed-bed cobalt-molybdenum catalyst, 4,000 psi hydrogen, and a temperature of 450 °C. The Homestead, Kentucky coal was slurried in coal-derived oil (35% by weight coal) and fed to the plant at 25 pounds per hour. A single sample of the liquid product was taken, separated into five portions, and stored in the refrigerator under nitrogen.

Twenty replicate determinations of asphaltenes were made with each test method, relying not only on written procedures but also on personal contacts with the authors of each method. Data collected include weight percent asphaltenes, insolubles, and oils. Standard deviations were calculated for each method and statistical comparisons made between methods.

The following are short descriptions of the five procedures studied:

Method A: A ten-gram sample is extracted with benzene in a Soxhlet apparatus. The benzene is removed on a steam bath, and 5 ml. of benzene are added to the residue. Asphaltenes are precipitated with 250 ml of n-pentane, and separated by filtration through the paper.

Method B: A three-gram sample is frozen and pulverized in liquid nitrogen and n-pentane is added. The sample is mixed and crushed while in an ultrasonic bath, and then centrifuged. The supernatant liquid is decanted into a rotary evaporator flask and the pentane washing procedure and centrifugation repeated three times. The combined supernatant solutions are then evaporated with nitrogen to recover the oil. Benzene is added to the insoluble material in the centrifuge tubes and the mixing, sonication, and centrifugation are carried out in the same manner as with the n-pentane. The supernatant benzene solutions are combined, evaporated under nitrogen, and finally freeze-dried to obtain the asphaltenes.

Method C: A three-gram sample is extracted under nitrogen with toluene in a Soxhlet apparatus. The toluene is removed from the extract in a rotary evaporator using a water aspirator. Exactly two ml of toluene per gram of soluble material are added

and the asphaltenes are precipitated with a volume of n-pentane equal to twenty times the volume of toluene that was added. The precipitate is then extracted with n-pentane in a Soxhlet apparatus.

Method D: Ten grams of sample are mixed with benzene, stirred for 30-60 minutes at 30 °C, and centrifuged. The benzene solution is decanted and the residue is washed with fresh benzene four times. The solvent is stripped from the combined supernatant liquid in vacuo at 30 °C, and finally the material is freeze-dried. The residue is dissolved in five ml. of benzene and the asphaltenes are precipitated with a liter of hexane. The solids are separated by centrifugation, the supernatant is stripped of hexane, and the precipitation procedure is repeated. The supernatants are combined and stripped as before, and the asphaltenes are freeze-dried.

Method E: A 25-gram sample is refluxed with benzene. The supernatant liquid is centrifuged and then filtered through paper under cover of nitrogen. The residue in the centrifuge tubes is refluxed with benzene, centrifuged, and filtered three more times. The collected extracts are evaporated under vacuum in a rotary evaporator at 105 °F. Cyclohexane is added to precipitate the asphaltenes and the mixture is refluxed under nitrogen. Centrifugation and filtration are carried out as above and are repeated once or twice depending on the color of the supernatant liquid. The reflux flask, centrifuge bottles, and filter paper are dried in vacuo and weighed to obtain the weight of the asphaltenes.

Table 1 shows the results obtained with the first three methods described above:

Table 1. - Results with Methods A, B, and C

	<u>% Insolubles ±1s</u>	<u>% Asphaltenes ±1s</u>	<u>% Oils ±1s</u>
Method A	5.2 ±0.3	26.9 ±0.7	67.9 ±0.7 (by difference)
Method B	7.6 ±0.5	23.8 ±0.7	67.2 ±0.9
Method C	4.6 ±0.5	22 ±2	70 ±3

The data indicate that the relative standard deviations for asphaltenes range from 2.6 to 6.8%, well within the range of acceptability for a separation procedure for coal-derived materials. There was considerable variation between methods in the length of time necessary to complete an analysis, in the amount of time expended by the analyst, and in the production rate.

In order to determine if the analytical results produced by each of the methods were significantly different, Student's 't' test was applied to the average of the 20 replicate analyses. Table 2 shows the findings obtained with the first three methods.

Table 2. - Significance* of Differences Between Methods

<u>Methods Compared</u>	<u>Insolubles</u>	<u>Asphaltenes</u>	<u>Oils</u>
A vs. B	Significant	Significant	Not significant
A vs. C	Significant	Significant	Not significant
B vs. C	Significant	Not significant	Not significant

*Student's 't' test - at the 95% confidence level.

It is evident that in half the comparisons made the difference proved to be significant. From the results obtained in this study one can surmise that the conclusions drawn from the comparison of the analyses of coal-derived liquids produced by different analytical procedures are problematical at best. One can also conclude that some acceptable "standard" method for the determination of asphaltenes in coal-derived liquids is urgently needed.